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ATOMIC SPECTROSCOPY

Laser Collinear Ionization of Accelerated Atoms in a Beam as a Method for Detecting Rare Isotopes of Krypton

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Abstract – Collinear laser photoionization of fast atoms via high-lying Rydberg states is proposed to be used for detecting rare isotopes of krypton. Experimental results are presented on the methods of two- and single-stage laser excitation of a krypton atom to a Rydberg state, and their comparative analysis is performed. It is shown that a simple scheme of Rydberg state population in a single stage satisfies the conditions necessary for detecting rare isotopes of Kr.

1. INTRODUCTION

1.1. Statement of the Problem

The development of an accessible method for detecting rare isotopes is of great interest for solving many problems of geophysics, oceanology, and environmental protection. In this paper, we dwell on the problem of detecting krypton isotopes. Along with stable krypton isotopes, two radioactive isotopes exist in nature. Krypton-85 (half-life of 10.8 years) is released into the atmosphere as a result of nuclear reactor operation. Its relative concentration in the atmosphere is at present $\sim 5 \times 10^{-11}$ (in relation to the stable isotopes). Krypton-81 (half-life of 2.13×10^5 years) is formed mainly in the upper layers of the atmosphere under the influence of cosmic rays as a result of the spallation reaction involving the stable isotopes of krypton as well as of neutron capture by the ^{80}Kr isotope. The relative concentration of ^{81}Kr is $\sim 5 \times 10^{-13}$. These isotopes can be used to determine the age of ground water and polar ice, study atmospheric flows, and detect solar neutrino fluxes.

Very high sensitivity and selectivity are required to measure such low concentrations. When a detection method based on radiative decay counting is used [1], samples of extremely large size are needed, particularly for ^{81}Kr. The method of accelerating mass-spectroscopy is inapplicable to inert gases, as they do not form negative ions (see [2] and references therein).

Over the last several years, researchers have paid a great deal of attention to the creation of a detector of ultrarare isotopes based on the selective action of laser radiation [3]. Several approaches were proposed to solve this problem: multistage isotope-selective photoionization of atoms [4], detection of photon flashes from thermal [5] and fast [6] atoms, observation of IR and UV fluorescence of molecules [7], selective cooling [8] and deflection [9] of thermal atoms, multistage resonant ionization in a fast atomic beam [10], selective dumping of an excited state [11], and resonant ionization at the mass-spectrometer input using CW lasers [12]. The potentials of some of the methods enumerated were demonstrated using stable isotopes of krypton. Thus, the dumping of the metastable $1s_5$-state of thermal atoms with a selectivity of 2.3×10^5 was realized [13]. The isotope-selective deflection of a collimated thermal beam of stable Kr atoms was demonstrated in [14]. The $1s_5 \longrightarrow 2p_9$ transition was used to produce a radiation force. The enrichment factor was 1.2×10^4. In [15, 16], observation of fluorescence and photon flashes was proposed for the detection of krypton isotopes. Significant progress was achieved in detecting ^{81}Kr by the method of resonant laser photoionization with preliminary mass selection [17]. In this method, isotope selectivity was ensured by repeated passages of ions through a mass filter, and laser radiation was used only for element-selective (i.e., nuclear charge-selective) ionization of a krypton atom at the input of a time-of-flight mass spectrometer. The given method allowed detection of krypton atoms in a sample at a relative concentration of ^{81}Kr down to 10^{-12}. The determination of the ^{81}Kr isotope concentration in a meteorite was realized as well [18]. In this case, the method of resonant ionization at the mass spectrometer input was employed, and the ratios ^{82}Kr/^{81}Kr $< 10^3$ could be determined.

1.2. Concept of the Method of Collinear Laser Photoionization

In the present work, the possibility of detecting krypton isotopes by the method of collinear laser ionization of atoms in an accelerated beam is examined. The concept of this method consists in the following [10]. Fast atoms produced by recharge of accelerated ions in a cell with alkali metal vapors are excited to a Rydberg state by laser radiation collinear to the accelerated beam. Then, the prepared atoms of a rare isotope are ionized as they fly into the electric field. The ions formed are deflected to a detector.

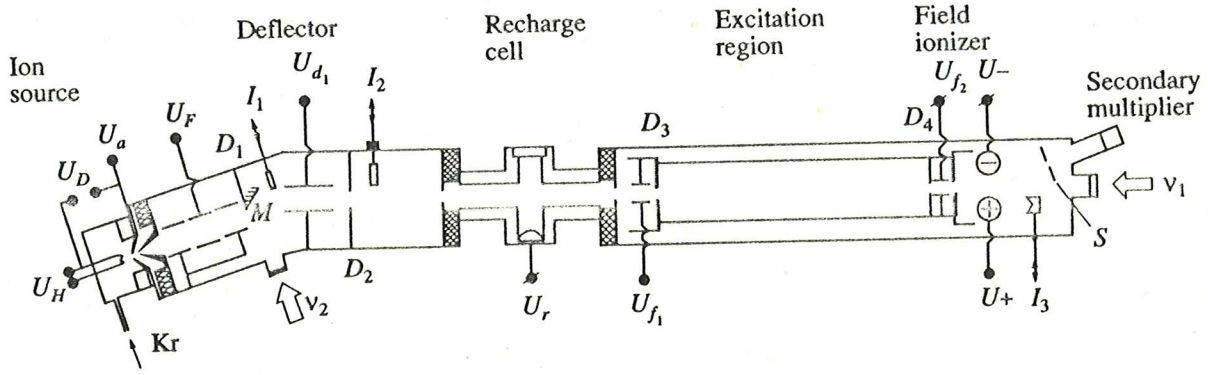

Fig. 1. Experimental layout: U_H, heating voltage of thermocathode; U_D, voltage for sustaining gas discharge; U_a, accelerating potential; U_F, potential of a single lens; U_{d_1}, voltage across the deflector; U_r, voltage across the recharge chamber; U_{f_1}, U_{f_2}, voltages across the filtering capacitors; $U+$ and $U-$, voltages applied to the ionizing cylinders; M, mirror; D_1 - D_4, apertures; I_1 - I_3, flux meters; S, slit.

In the collinear geometry of atomic beam excitation [19], an additional isotopic shift appears

$$|\delta| \simeq (\nu/c)\sqrt{(2eU_a)}\,(1/\sqrt{M_1} - 1/\sqrt{M_2}), \quad (1)$$

where ν is the atomic transition frequency, c is the velocity of light in a vacuum, eU_a is the kinetic energy of fast atoms, and M_1 and M_2 are the isotope masses. At $eU_a = 10$ keV, the value of δ can exceed the natural isotopic shift by a factor of several tens. The absorption linewidth decreases considerably as a consequence of the velocity bunching effect in the accelerated beam [19]. It is determined by the following expression:

$$\Delta\nu_D \simeq (v/c)\,\nu\,(\Delta U_a/2U_a), \quad (2)$$

where $v = \sqrt{(2eU_a/M)}$ is the velocity of fast atom motion, and $e\Delta U_a$ is the spread of kinetic energies of atoms in the beam.

Successful test experiments were performed on isotope-selective ionization of accelerated atoms of potassium [20] and helium [21]. The collinear laser photoionization method enabled detection of the helium-3 rare isotope at relative concentrations down to 10^{-9} [22].

2. PRODUCTION OF FAST KRYPTON ATOMS IN METASTABLE STATES

A collinear and sufficiently monoenergetic beam of atomic particles is required to realize the method of collinear laser photoionization. In experimental physics, collimated beams of atomic ions generated by the ionization of atoms in an ion source and the subsequent acceleration of the ions in electric field are widely used. In gas-discharge ion sources working with inert gases, a spread of ion energies less than 1 eV can experimentally be obtained in a beam [23]. Such a spread in energy corresponds to a residual Doppler broadening $\Delta\nu_D \leq 20$ MHz for a Kr beam with an energy of 5 keV at $\lambda = 5000$ Å [see (2)].

Photoionization in a beam of single-charged atomic ions is possible in principle, but the energy needed to ionize an atomic ion is very high as a rule, and absorption spectrum lines lie in the ultraviolet range. This makes realization of stepwise resonant photoionization in an atomic beam a technically difficult problem. It is much easier to achieve resonant laser photoionization in an accelerated monoenergetic atomic beam, which can be obtained from an ionic beam via neutralization. In this case, the photoions formed can be easily extracted from the beam with the help of the electric field.

For the neutralization of ionic beams, the phenomenon of quasi-resonance ion recharge in alkali metal vapor is widely used. As a result of this process, accelerated atoms are formed mainly in quantum states with an electron bond energy approximately equal to the energy in the alkali metal atom at which the recharge occurred. Therefore, the efficient population of high-lying metastable states and production of accelerated beams of metastable atoms are found to be possible [24]. This is of particular importance for atoms of inert gases, as hard ultraviolet radiation is needed for laser excitation from the ground state.

A diagram of the experimental setup used in studies of collinear laser photoionization of krypton atoms is described in detail in [21, 25] and shown in Fig. 1. A beam of krypton ions accelerated to an energy $eU_a = 3$ keV was produced with the help of a gas-discharge source with a hot cathode. It was focused by a single electrostatic lens and deflected by a deflector d_1. Such deflection made it possible to eliminate the neutral component of the ionic beam as well as to introduce laser radiation in pursuit of the deflected beam with the help of a mirror M. Then, the ionic beam entered a recharge chamber with potassium vapor at a temperature of 160°C, where about half the ions were recharged to neutral atoms. The kinetic energy of formed neutral atoms of krypton is equal to $e(U_a - U_r)$, where U_r is the potential of the recharge chamber. Nonrecharged ions and atoms in highly excited states were removed from the beam using a filtering capacitor f_1, and the beam of fast atoms arrived at the region of laser excitation of length $l = 1$ m shielded from electric

fields, where pulsed resonant laser excitation of metastable krypton atoms to a Rydberg state was realized. The laser radiation was introduced to the excitation region strictly collinear with the accelerated atomic beam. Upon leaving the excitation region, Rydberg atoms were ionized as they flew into the electric field of two oppositely charged cylinders $U+$ and $U-$ and deflected by the same field through an adjustable slit S to a secondary electron multiplier. The flow of neutral krypton atoms, measured at the output of the system (the aperture D_4 had a diameter of 2 mm) by a detector based on secondary electron emission, was 10^{11} at/s.

The krypton atom has two high-lying metastable states, $1s_5(5s[3/2]_2^\circ)$ and $1s_3(5s'[1/2]_0^\circ)$, which are populated as a result of the quasi-resonance recharge. It was interesting to compare the magnitudes of photoion signals resulting from excitation of atoms from these states. In this case, laser two-stage excitation occurred through one and the same intermediate level $2p_3(5p'[1/2]_1)$ (Fig. 2), and the conditions of the excitation at the second stage ($\lambda_2 \simeq 6760$ Å) were kept constant. Saturation of the atomic transition was provided at the first stage ($\lambda_1 \simeq 5570, 7855$ Å).

If we assume that the metastable states $1s_5(5s[3/2]_2^\circ)$ and $1s_3(5s'[1/2]_0^\circ)$ in the process of recharge were populated in proportion to their statistical weights (5 : 1), then the ratio of the photoion signals should be 3 : 1 for the excitation by linearly polarized laser light, as the states of the $1s_3$ level with $|M_J| = 2$ cannot be excited by linearly polarized light to the $2p_3$ level with $J = 1$. It was observed experimentally that the photoion signal resulting from the excitation from the $1s_5$ state was 2.9 ± 0.5 times greater than in the case when the excitation occurred from the $1s_3$-state.

3. PHOTOIONIZATION OF FAST ATOMS VIA RYDBERG STATES

In the process of accelerated atomic beam propagation in a vacuum system, collisional ionization of fast atoms by residual gas molecules takes place. The cross section of this process is rather significant, $\sigma_{01} \sim 10^{-16}$ cm^2 [26]. At a pressure of 10^{-8} torr in the vacuum system (the number density of residual gas molecules is $n \simeq 3.5 \times 10^8$ cm^{-3}), a fraction $\alpha = \sigma_{01} nl \simeq 3.5 \times 10^{-6}$ of accelerated atoms will be ionized at a length of $l = 1$ m. Such ions, unrelated to laser radiation, will be detected together with ions formed in the interaction region during photoionization of atoms to continuum or through autoionization levels. In this case, the isotopic selectivity S of atom photoionization will be confined by the background signal at a level clearly insufficient to detect rare isotopes ($S < 1/\alpha \simeq 2.8 \times 10^5$).

Significant background signal suppression may be achieved if atoms are ionized via a Rydberg state. Then, accelerated atoms resonantly excited to a Rydberg state are ionized at the output from the excitation region upon flying into a constant electric field of an ionizer. As opposed to ions, Rydberg atoms in an electric field

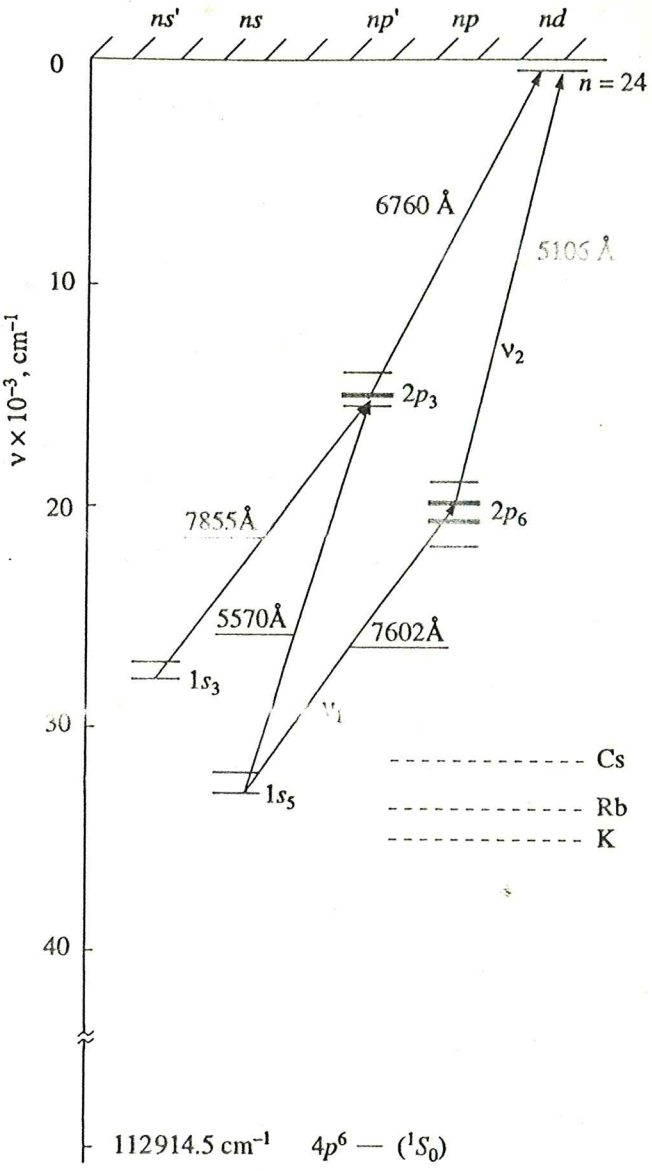

Fig. 2. Kr atom energy levels and two-stage schemes of excitation to Rydberg states.

do not experience kinetic acceleration to the point of ionization. As a consequence, a photoion path may differ significantly from that of an ion formed in the excitation region.

For instance, photoions produced in a transverse electric field formed by two cylindric electrodes of opposite charge (Fig. 1) are deflected at a considerably smaller angle than ions from the excitation region. Inasmuch as different Rydberg states are ionized at different electric field strengths, such ionization layout possesses angular dispersion in the principal quantum number n [21]. If the slit S is adjusted in such a way that the scheme detects photoions coming from a small spatial domain in electric field, where field ionization of signal Rydberg atoms occurs, then suppression of the collisional background by several orders can be ensured.

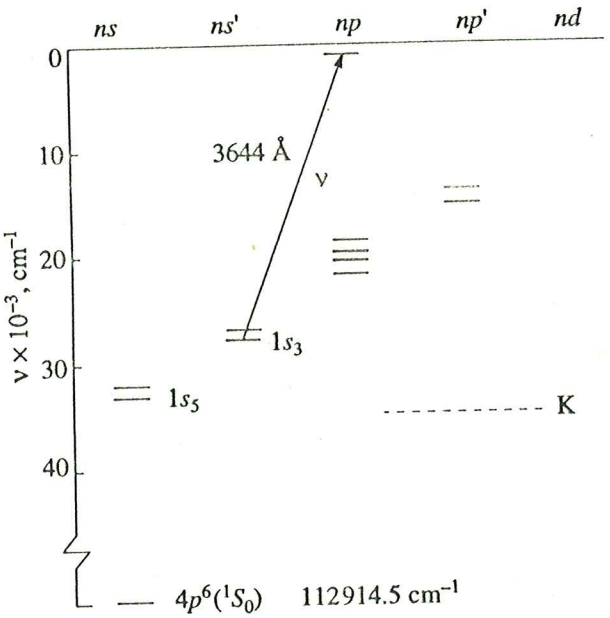

Fig. 3. Kr atom energy levels and single-stage scheme of excitation to a Rydberg state.

Apart from collisional ionization, collisional excitation of accelerated atoms to Rydberg states contributes to the background signal as well. The collisional excitation cross section is much smaller than the collisional ionization cross section [26, 27]. However, collisionally excited Rydberg atoms are formed over the entire length of the excitation region as a fast beam propagates.

In experiments with accelerated krypton atoms at a pressure of 3×10^{-7} torr in the vacuum system, the background signal level was 8×10^{-8} of the neutral atom flow and could be diminished down to 3×10^{-11} with vacuum improving to 10^{-10} torr. Nevertheless, such a background signal level is too high for detecting rare isotopes of krypton.

For a radical suppression of the background signal, preliminary mass separation of isotopes in the accelerated ion beam should be used. Thus, for instance, a magnetic mass separator placed along the beam path between the ion source and the recharge cell can decrease the total current associated with abundant isotopes, and consequently the background signal, by a factor of 10^4 - 10^7, leaving the flow of rare isotope atoms through the system unchanged.

4. SCHEMES OF POPULATING RYDBERG STATES OF A KRYPTON ATOM

Let us consider three possible schemes of laser photoionization of a krypton atom. The first two schemes are two-stage. In one scheme ($\lambda_1 \simeq 7602$ Å, $\lambda_2 \simeq 5106$ Å, Fig. 2), the green line of a copper vapor laser (CVL) is proposed to populate Rydberg states of a krypton atom accelerated to a certain energy. Here, narrow-band laser radiation should be used at the first stage. In another scheme, the utilization of a narrow-band laser at both steps ($\lambda_1 \simeq 5570$ Å, $\lambda_2 \simeq 6760$ Å, Fig. 2) provides an increase in the photoexcitation selectivity as compared to the first scheme. The third scheme is single-stage ($\lambda \simeq 3644$ Å, Fig. 3). An isotope-selective population is assumed to be performed using the second harmonic of CW semiconductor laser radiation ($\lambda \simeq 7300$ Å) preamplified in a pulsed laser amplifier pumped by a CVL.

The schemes listed above are assumed to utilize pulsed laser radiation. This is dictated by the fact that a drop in the selectivity of rare isotope photoexcitation takes place during the transition to the CW mode. This drop is related to ionization of abundant isotope atoms by the ionizer electric field in the presence of laser radiation.

Each scheme will be characterized by the following parameters: the experimentally measured pulse energy density providing saturation of the atomic transition used, E_{sat}; the maximum number of photoion counts N detected in a single laser pulse normalized to the total number of atoms residing in the excitation region at the instant of the laser pulse; the potential isotope selectivity S of resonant ionization calculated from [28, 29]; the expected photoion counting rate Q_c for a rare isotope; and the detected background signal Q_b due to collisions of fast atoms with residual gas.

Let us consider the question concerning the maximum number of photoions that can be detected in a single laser pulse. After passing through the recharge cell, only a certain portion of atoms η_{rec} is in the required metastable state. If population of lower states, whose bond energy is close to the ionization potential of potassium atom, proceeds proportionally to their statistical weights g_i, then $\eta_{rec} \simeq g_{met}/\sum g_i$, where g_{met} is the statistical weight of the metastable level used. Under the influence of laser radiation, only a certain portion of atoms η_{exc} may be transferred to a Rydberg state. If the atomic transitions used are saturated, this portion is $\eta_{exc} \simeq g_f/\sum g_K$, where g_f is the degeneracy multiplicity of the Rydberg level and $\sum g_K$ is the sum of degeneracies of all the levels used. The radiative decay of the intermediate level to nonresonant states during laser excitation will cause a decrease in the photoion signal. This decrease is denoted by the factor η_{int}. The next factor $\eta_{del} = \exp(-t_{del}/T_2)$, where T_2 is the lifetime of the intermediate level, is conditioned by the delay time t_{del} between the laser pulses of the first and the second stages. Owing to the finite radiative lifetime of the Rydberg atom state T_f in comparison with the time of flight through the excitation region $\tau = l/v$, the atoms do not all have a chance to reach the field ionizer in the state f. The portion of atoms in the Rydberg state f flying to the region of field ionization is $\eta_{rad} \simeq (1/\tau)\int^{\tau} \exp(-t/T_f)\,dt = (T_f/\tau)[1 - \exp(-\tau/T_f)]$. The last factor η_{det} is related to the detector efficiency (a secondary multiplier in our case). As a result, the maximum number of photoion counts that can be recorded in a single laser pulse normalized to the number of atoms residing in the excita-

tion region at the instant of a laser pulse is determined by the following expression:

$$N \simeq \eta_{rec}\eta_{exc}\eta_{int}\eta_{del}\eta_{rad}\eta_{det}. \quad (3)$$

It is expedient to consider the question of laser excitation selectivity taking a two-level system as an example. It was shown theoretically in [28, 29] that the excitation of a two-level system of an isolated particle by laser radiation of frequency ν detuned from the resonance by δ proceeds with absorption of two photons simultaneously from the light wave and spontaneous reemission of a photon of energy $h(\nu - \delta)$. The selectivity S of rare isotope photoionization, when the simultaneous effect of the laser optical field and the electric field of the ionizer upon the atom is excluded, is determined by the expression [28, 29]

$$S \sim (\hbar\delta_{is}/\mu E)^4(\Gamma\tau_p)^{-1}, \quad (4)$$

where μ is the electric dipole moment of the atomic transition, E is the electric field strength of the light wave, δ_{is} is the isotopic shift, Γ is the homogeneous absorption linewidth, and τ_p is the laser pulse width ($\tau_p < 1/\Gamma$). For this mechanism of upper level population, the latter depends on detuning as δ^{-4}.

At a rate of rare isotope excitation of the order of the inverse pulse width, i.e. $(\mu E/2\hbar)\tau_p \sim 1$, the selectivity is

$$S \simeq (\delta/\Gamma\,[\mathrm{MHz}])^4(\Gamma\,[\mathrm{s}^{-1}]\tau_p)^3. \quad (4a)$$

It should be noted that a formula for a Lorentzian profile is sometimes mistakenly used to estimate the excitation probability W of a two-level system in the line wing ($\delta \gg \Gamma$):

$$W \simeq (\Gamma/\delta)^2(\Gamma\tau_p)^{-1}. \quad (5)$$

This formula actually describes resonance scattering of photons by an isolated two-level system. It holds for estimating the excitation probability only for a two-level system in a thermostat, where the energy defect may be transferred to the environment of the two-level particle. Formula (5) underestimates the excitation selectivity in comparison with (4).

Let us turn to three-level atomic systems. Here, two cases are possible: when laser pulses act simultaneously on an atom, and when the pulses do not substantially overlap in time.

Let Γ_{21} and Γ_{32} be the spontaneous decay rates for the first and the second atomic transitions, respectively; $\delta_1 \gg \Gamma_{10}$ and $\delta_2 \gg \Gamma_{21}$ are the laser field frequency detunings from exact resonances. In the first case, the excitation probability W of an isolated three-level system by laser radiation with sufficiently large detuning from the two-photon resonance, $|\delta_1 + \delta_2|^{-1} \ll \tau_p$ is determined by the following expression [29]:

$$W \simeq (F_{12}^4F_{23}^2\Gamma_{21}\tau_p + F_{12}^2F_{23}^4\Gamma_{32}\tau_p)/(\delta_1^2\delta_2^2[\delta_1+\delta_2]^2), \quad (6)$$

where $F_{12} = \mu_{12}E_1/2\hbar$, $F_{23} = \mu_{23}E_2/2\hbar$ are the matrix elements of the operator of interaction between the atomic system and laser radiation.

At $F_{12}, F_{23} \sim \tau_p^{-1}$ and $\Gamma_{32}\tau_p \ll 1$, the selectivity is equal to

$$S \simeq W^{-1} \simeq (\delta_1^2\delta_2^2[\delta_1+\delta_2]^2/\Gamma_{21}\,[\mathrm{MHz}])^6 \times (\Gamma_{21}\,[\mathrm{s}^{-1}]\tau_p)^5. \quad (6a)$$

As shown in [29], in the second case the probability of excitation W of an isolated three-level system by laser radiation reduces to a mere multiplication of excitation probabilities of two two-level systems

$$W \simeq [(F_{12}^4/\delta_1^4)\Gamma_{21}\tau_p]\,[(F_{23}^4/\delta_2^4)\Gamma_{32}\tau_p]. \quad (7)$$

In this case, at $F_{12}, F_{23} \sim \tau_p^{-1}$, the selectivity is equal to

$$S \simeq [(\delta_1/\Gamma_{21}\,[\mathrm{MHz}])^4(\Gamma_{21}\,[\mathrm{s}^{-1}]\tau_p)^3] \times [(\delta_1/\Gamma_{21}\,[\mathrm{MHz}])^4(\Gamma_{21}\,[\mathrm{s}^{-1}]\tau_p)^3]. \quad (7a)$$

Evidently, if an atom is irradiated by laser pulses separated in time, the excitation selectivity is much higher than in the case of simultaneous action of pulses. However, in the former case, the photoion signal decreases owing to radiative deexcitation of the intermediate level during the delay time between laser pulses.

Parameters of hyperfine splitting for rare isotopes of krypton are unknown for the transitions used. Therefore, the isotope shift was estimated from the expression for an artificially produced isotope shift [see (1)].

The next important parameters of the rare isotope detection scheme are the expected counting rate of rare isotope photoions and the recorded background signal associated with collisions of fast atoms of the main isotope with residual gas. These parameters are very important, inasmuch as for a reliable detection of a rare isotope one should have, apart from sufficient selectivity, a counting rate of rare isotope photoions exceeding the collisional background signal. At the total current of all krypton isotopes I at the mass separator input, the absolute current of ions of a rare isotope with a concentration C will be IC. Then, the flow of fast ions of the rare isotope downstream from the recharge cell will be IC/k, where k is the factor allowing for losses in both the mass separator and the recharge cell. This results in a counting rate of rare isotope photoions equal to

$$Q_c \simeq (Ic/k)(N\tau f), \quad (8)$$

where f is the laser pulse repetition rate.

The recorded background signal arising from collisions of fast atoms of the main isotopes with residual gas will be

$$Q_b \simeq (I/S_{m-s}k)(q\tau f), \quad (9)$$

where S_{m-s} is the enrichment of the ionic beam in the rare isotope provided by the mass separator, q is the collisional background signal in the continuous mode normalized to the current of fast atoms, and τ is the time of flight through the excitation region.

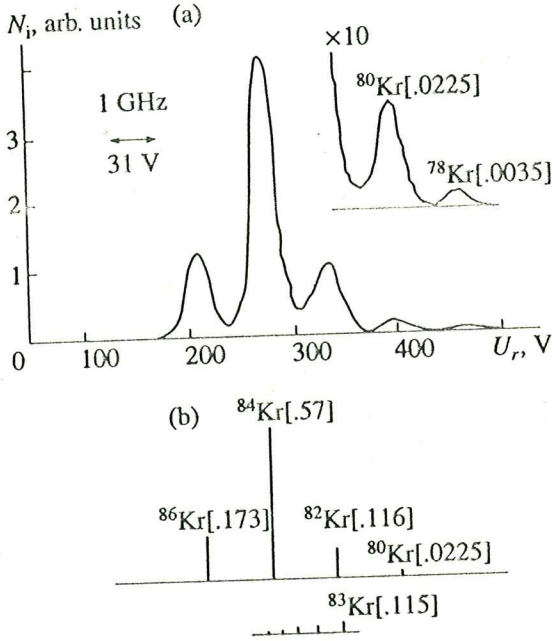

Fig. 4. (a) Ion signal N_i obtained with excitation of natural mixture of Kr isotopes according to a two-stage scheme ($\lambda_1 \simeq 7602$ Å, $\lambda_2 \simeq 5106$ Å) as a function of the potential applied to the recharge chamber U_r; (b) calculated positions of resonances of a monoenergetic beam of Kr atoms with narrow-band laser radiation ($\lambda_2 \simeq 5106$ Å).

4.1. Two-Stage Scheme Utilizing the Green 5106 Å Line of a Copper Vapor Laser (CVL) at the Second Stage

The employed scheme of two-stage excitation of a krypton atom from the metastable state $5s[3/2]_2(1s_5)$ to the Rydberg state $24d[3/2]_2$ is shown in Fig. 2. In the experiment on measuring efficiency and performing isotope-selective photoionization of krypton atoms via the intermediate level $2p_6$, the green CVL line (5106 Å) was used at the second stage of laser excitation, and radiation of a dye laser ($\Delta\nu_1 \simeq 1$ cm^{-1}) pumped by the yellow CVL line (5782 Å) was used at the first stage. In the experiment, we succeeded in saturating both stages of laser excitation. The energy densities in the laser pulses $E_{sat1} \simeq 3.8$ μJ/cm^2 and $E_{sat2} \simeq 7.3$ mJ/cm^2 provided saturation of the atomic transitions used at the first and the second stage, respectively. The CVL radiation was introduced in the same direction as the fast atomic beam, while the dye laser radiation was introduced in the opposite direction. The laser pulse repetition rate was $f \simeq 8.6$ kHz, their width $\tau_p \simeq 15$ ns, and the time delay between the pulses $t_{del} \simeq 6$ - 12 ns in the excitation region.

The Doppler frequency shift in the absorption spectrum of the fast atomic beam is determined by the expression

$$|\Delta\nu| = (\nu/c)\sqrt{[2e(U_a - U_r)/M]}, \qquad (10)$$

where ν is the atomic transition frequency, c is the velocity of light in a vacuum, $e(U_a - U_r)$ is the kinetic energy of fast atoms (U_a is the accelerating voltage, U_r is the voltage applied to the recharge chamber), and M is the atomic mass. The green CVL line could be brought to resonance with an atomic transition to a certain Rydberg state by an appropriate selection of atomic beam energy. For our installation, it was technically more suitable to excite the $24d[3/2]_2$ state. This could be accomplished at a beam energy $e(U_a - U_r) \simeq 2.7$ keV. For this purpose, green CVL line radiation was collimated by a telescope and directed by a mirror M (Fig. 1) in pursuit of the atomic beam.

When both stages of laser excitation were saturated, about 4% of accelerated krypton atoms were detected as photoions. In the experiment, the signal was collected not from the entire excitation region but only from a region 0.63 m long corresponding to a time of flight $\tau \simeq 8$ μs. According to formula (3), the maximum number of photoion counts that can be recorded in a single laser pulse, normalized to the total number of atoms, is $N \simeq \eta_{rec}\eta_{exc}\eta_{int}\eta_{del}\eta_{rad}\eta_{det}$. If we assume that the near-resonance $1s_2$, $1s_3$, $1s_4$, and $1s_5$ states are predominantly populated in quasi-resonance recharge, then $\eta_{rec} \simeq 5/12$ of all the atoms should be at the $1s_5$ level. If atoms are excited by linearly polarized light and the atomic transitions are saturated, then $\eta_{exc} \simeq 1/3$. In the absence of time delay between excitation pulses at the first and the second stages, we have $\eta_{del} = 1$. The factor η_{int} is ≃0.9. At a lifetime of the Rydberg state $T_f \simeq 6$ μs [30] and a collection time $\tau \simeq 8$ μs, we have $\eta_{rad} \simeq 0.55$. The detection efficiency of the secondary multiplier is $\eta_{det} \simeq 0.69$. As a result, we obtain $N \simeq 4.7\%$ for a signal from the excitation region, in agreement with the measurement results.

Two Fabry–Perot interferometers with 10- and 30-mm bases were placed normal to the laser beam at the input to the vacuum system in order to narrow the CVL radiation spectrum. Then, the interferometers were tuned to maximum transmission of laser radiation. The photoion signal N_i is shown in Fig. 4a as a function of the recharge chamber potential U_r. Figure 4b shows the calculated relative positions and the intensities of absorption lines of the fast atomic beam, which are determined by its isotopic structure. The calculation of the hyperfine structure of the odd isotope ^{83}Kr was performed using the parameters A and B given in [31]. Note that it is not possible to obtain high isotopic selectivity if such radiation is used to excite atoms of rare isotopes, as the radiation spectrum width is large.

For highly selective laser excitation of rare isotopes of krypton, narrow-band radiation should be used at the first stage. Such radiation can be generated by a CW single-frequency dye laser (7602 Å) and amplified in a pulsed amplifier pumped by CVL radiation. At a laser pulse width $\tau_p \simeq 15$ ns, the spectrum width of an amplified pulse will be $\Delta\nu_1 \geq 1/2\pi\tau_p \simeq 11$ MHz, making it possible to readily saturate the atomic transition at the first stage. The energy density in a laser pulse, ensuring saturation of the atomic transition, will be $E_{sat} \simeq 3.8$ nJ/cm^2 in this case.

At the second stage of laser excitation, broad-band radiation ($\Delta\nu_2 \simeq 0.2$ cm^{-1}) of the green CVL line is

used. Therefore, laser pulses of the first and the second stages should be separated in time by $t_{del} \geq 20$ ns in order to exclude two-photon resonance with respect to the widespread isotope of krypton. Then, the photoexcitation selectivity calculated from formula (4a) will be $S \simeq 2.2 \times 10^7$ at an isotope shift $\delta_1 \simeq 0.63$ GHz.

If the ion current is enriched in a rare krypton isotope by a factor $S_{m-s} \simeq 10^5$ owing to preliminary mass separation, then the optical selectivity required to detect ^{81}Kr and ^{85}Kr is 2×10^7 and 2×10^5, respectively. The estimate of the two-stage excitation selectivity listed above satisfies this requirement.

Let us calculate the normalized value of the maximum number of photoion counts in a single laser pulse from formula (3): $N \simeq \eta_{rec}\eta_{exc}\eta_{int}\eta_{del}\eta_{rad}\eta_{det}$. It should be noted that when metastable atoms are excited by narrow-band radiation, the initial level is an individual component of the hyperfine structure of a rare isotope. For ^{81}Kr with a nuclear spin of 7/2, the probability of recharge to the component with a moment $F = 11/2$ is $\eta_{rec} \simeq 1/8$. The probability of laser excitation by laser pulses separated in time is $\eta_{exc} \simeq 3/8$. Correspondingly, for ^{85}Kr with a nuclear spin of 9/2, we have $\eta_{rec} \simeq 7/60$ and $\eta_{exc} \simeq 3/8$. The factor η_{int} is about 0.8. The factor arising from a 20-ns delay between laser pulses of the first and the second stages is $\eta_{del} \simeq 0.46$. The time of flight of a krypton atom through a region of length 1 m at an energy $eU_a = 2.7$ keV is $\tau \simeq 12.6$ μs. Therefore, $\eta_{rad} \simeq 0.42$. The detection efficiency of the secondary multiplier is $\eta_{det} \simeq 0.69$. As a result, we have $N \simeq 5.4 \times 10^{-3}$ for ^{81}Kr and $N \simeq 5 \times 10^{-3}$ for ^{85}Kr.

Let the total current of all krypton isotopes at the mass separator input be $I = 10^{13}$ s^{-1} (1.6 μA). Then, the photoion counting rate calculated from formula (8) is at a level of 4.1 counts per hour for ^{81}Kr and 380 counts per hour for ^{85}Kr, if the loss in the absolute current of a rare isotope in the mass separator and the recharge cell is described by a factor $k = 3$. As shown earlier in Section 3, the background signal due to collisions of fast atoms of the main isotope with residual gas constitutes approximately a fraction $q = 8 \times 10^{-8}$ of the fast atom flow at a pressure of 3×10^{-7} torr in the installation. Then, at a residual gas pressure of 10^{-10} torr, the background signal calculated from formula (9) will be at a level of 0.4 counts per hour, permitting reliable detection of rare isotopes of krypton.

4.2. Two-Level Scheme Utilizing a Narrow-Band Radiation at Both Stages

The utilization of a narrow-band radiation at both stages of laser excitation will allow one to obtain an acceptable magnitude of the optical selectivity even in the absence of a delay between laser pulses.

We propose a two-stage scheme for krypton atom excitation from the metastable level $5s[3/2]_2(1s_5)$ to the Rydberg state $24d[3/2]_2$ shown in Fig. 2 ($\lambda_1 \simeq 5570$ Å, $\lambda_2 \simeq 6760$ Å). Narrow-band radiation can be generated by CW single-frequency dye lasers with subsequent amplification in pulsed CVL-pumped amplifiers. In this case, the spectral width of the amplified radiation will be $\Delta\nu_1 \geq 1/2\pi\tau_p \simeq 11$ MHz ($\tau_p \simeq 15$ ns). This easily enables the saturation of the atomic transitions at both stages. The energy densities in laser radiation pulses providing saturation of the atomic transitions used are $E_{sat1} \simeq 4$ nJ/cm^2 and $E_{sat2} \simeq 40$ μJ/cm^2 at the first and the second stages, respectively.

The isotope shifts at an energy $eU_a = 4$ keV estimated from formula (1) are $\delta_1 \simeq 1$ GHz and $\delta_2 \simeq 0.9$ GHz. In this case, the selectivity of photoionization calculated according to (6a) is $S \simeq 3 \times 10^{12}$. This exceeds the value of the optical selectivity required to detect rare isotopes of krypton in combination with mass separator at $S_{m-s} = 10^5$. It should be noted that the excitation selectivity can be significantly increased using laser pulses separated in time.

According to (3), the normalized maximum number of photoion counts per single laser pulse is $N \simeq 2.2 \times 10^{-2}$, which is four times greater than the factor N in Section 4.1. Therefore, the photoion count rate calculated in analogous conditions will be at a level of 14 and 1400 counts per hour for ^{81}Kr and ^{85}Kr, respectively. At a pressure of 10^{-10} torr in the vacuum unit, the background signal will be about 0.5 counts per hour and will permit reliable detection of both ^{81}Kr and ^{85}Kr.

4.3. Simple Single-Stage Scheme of Excitation of the Krypton Atom Rydberg Level

The optical selectivity of resonance ionization at a level of 10^{10} can be obtained using only one stage of excitation directly from a metastable state to a Rydberg one. In many cases, for instance, for noble gases, the presence of high-lying metastable states allows a single-stage population of a Rydberg state to be performed using available lasers.

To prepare krypton atoms in a Rydberg state in the experiment, a Rydberg state was excited according to the scheme $1s_3(5s'[1/2]_0) \longrightarrow np_1(n^* \simeq 21)$ (Fig. 3). The metastable state $1s_3$ is efficiently populated in quasi-resonance recharge of accelerated krypton ions in potassium vapors. The measurements were made on a beam of krypton atoms at an energy $eU_a = 3.9$ keV (Fig. 1).

The excitation of fast krypton atoms was realized using a dye laser pumped by an excimer XeCl laser with 16-Hz pulse repetition rate. The spectral width of laser radiation ($\lambda \simeq 3644$ Å) was $\Delta\nu \simeq 0.5$ cm^{-1}. At an energy density in a pulse $E \simeq 120$ μJ/cm^2, a portion $N \simeq 5.9 \times 10^{-5}$ of accelerated atoms that were present at the output of the field-free region were detected as photoions. Unfortunately, the energy of a laser pulse was insufficient to saturate the atomic transition used. However, the saturation energy density E_{sat} of the atomic transition can be determined from formula (3)

$$N = \eta_{rec}\eta_{exc}\eta_{in}\eta_{rad}\eta_{det},$$

where $\eta_{rec} \simeq 1/12$ is the probability that a recharged atom appears in the metastable state $1s_3$; $\eta_{exc} \simeq 1/2$ is the probability of laser excitation of an atom to a Rydberg state provided that the atomic transition is saturated by

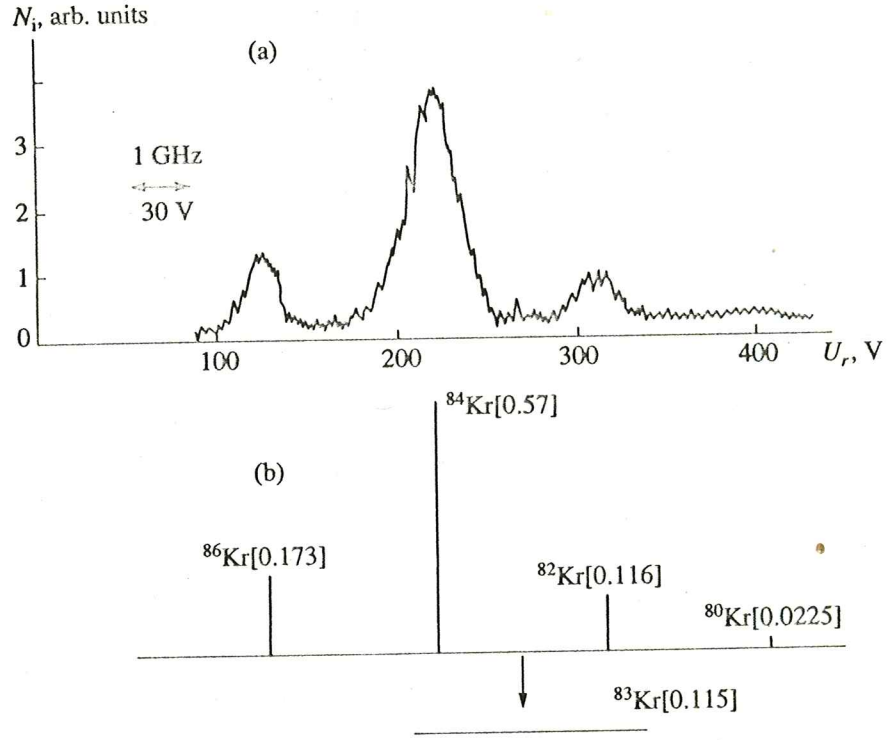

Fig. 5. (a) Ion signal N_i obtained with excitation of natural mixture of krypton isotopes according to a single-stage scheme ($\lambda \simeq 3644$ Å) as a function of the potential applied to the recharge chamber U_r; (b) calculated positions of resonances of a monoenergetic beam of Kr atoms with narrow-band laser radiation ($\lambda \simeq 3644$ Å).

linearly polarized radiation; $\eta_{in} \simeq [1 - \exp(-E/E_{sat})]$ is the factor allowing for the probability of Rydberg level population as a function of laser pulse energy density E; $\eta_{rad} \simeq (T_f/\tau)[1 - \exp(-\tau/T_f)]$, where T_f is the Rydberg level lifetime, τ is the time of atom flight from the point where it is excited by laser radiation to the point of field ionization; and $\eta_{det} \simeq 0.69$ is the efficiency of the secondary multiplier. If $E \ll E_{sat}$, $1 - \exp(-E/E_{sat}) \simeq E/E_{sat}$. The condition $\tau \ll T_f$ was provided in the measurements of the photoion signal, hence $\eta_{rad} \simeq 1$. As a result, we obtain $E_{sat} \simeq 58$ mJ/cm^2 at $\Delta\nu \simeq 0.5$ cm^{-1}. From the analysis of temporal shape of the photoion signal, one may estimate a lifetime of a Rydberg state $T_f > 2.6$ μs.

To observe various krypton isotopes, the spectrum of laser radiation was narrowed with the help of an external Fabry–Perot etalon with 0.5 cm^{-1} free spectral range. In this case, the spectrum width was 0.04 cm^{-1}. Fine tuning to resonance with absorption lines of various isotopes was realized by varying the decelerating voltage U_r across the recharge cell. The photoion signal N_i as a function of voltage U_r is shown in Fig. 5a. The calculated relative positions and intensities of resonances of a Kr beam ($eU_a = 3.9$ keV) with natural isotope content are presented in Fig. 5b. The parameters A and B are unknown for the upper Rydberg state of ^{83}Kr.

For highly selective excitation of rare isotopes of krypton ^{81}Kr and ^{85}Kr, with relative concentrations 5×10^{-13} and 5×10^{-11}, respectively, narrow-band laser radiation can be obtained according to the following scheme. The light from a CW semiconductor laser with a wavelength $\lambda \simeq 7300$ Å is amplified in a dye laser amplifier pumped by a CVL with a pulse repetition rate $f = 10$ kHz and a pulse width $\tau_p = 15$ ns and then directed to a frequency-doubling crystal. At a laser radiation spectrum width $\Delta\nu \simeq 1$ MHz ($\Delta\nu \geq 1/2\pi\tau_p$), the energy density in a pulse E_{sat} needed to saturate the atomic transition is $E_{sat} \simeq 35$ μJ/cm^2. This value is very close to the saturation energy density given in Section 4.2.

The optical selectivity is calculated from formula (4a). At an isotope shift $\delta \simeq 1.6$ GHz, a laser pulse width $\tau_p = 15$ ns and a spontaneous decay rate of the Rydberg level $\Gamma = 0.03$ MHz (1.7×10^5 s^{-1}), the selectivity is $S \simeq 10^{11}$. The presented estimate of the single-stage excitation selectivity considerably exceeds the required value when a mass separator is used.

According to formula (3), $N \simeq 2 \times 10^{-2}$. This value virtually coincides with the analogous value obtained for the two-stage scheme in Section 4.2. Under the conditions described in previous sections, the photoion counting rate calculated from formula (8) is 13 and 1300 counts per hour for ^{81}Kr and ^{85}Kr, respectively. As shown above, this ensures reliable detection of rare isotopes of krypton (the background signal is at a level of 0.4 counts per hour).

5. CONCLUSION

The estimates presented show that the proposed method of collinear laser photoionization of fast atoms in combination with preliminary mass enrichment of

the ionic beam in a rare isotope at a level of 10^5 should allow reliable detection of rare isotopes of krypton. At an ion current $I = 10^{13}$ s^{-1} (1.6 μA), the time required to count 10 photoions of a rare isotope at the input to a mass separator is 0.5 and 45 min for ^{85}Kr and ^{81}Kr, respectively.

Among the considered schemes of laser excitation of a krypton atom to a Rydberg state, the single-stage scheme is distinguished for its simplicity and high selectivity in comparison with the two-stage scheme utilizing broad-band radiation at the second stage. It should be noted that an analogous scheme of single-stage excitation can be utilized for detecting rare isotopes of other noble gases.

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